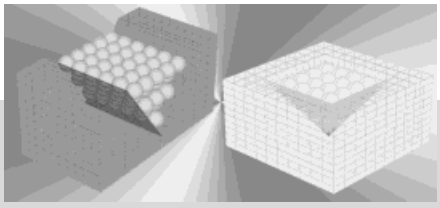
The Race for the Photonic Chip: Colloidal Crystal Assembly in Silicon Wafers**

By *Geoffrey A. Ozin** and *San Ming Yang*



This paper surveys recent developments in engineering physics approaches and self-assembly chemistry methodologies for creating 3D photonic crystals and how this has led to in-wafer patterned colloidal crystals. These materials are comprised of single crystal micrometer scale features of silica colloidal crystals that have controlled thickness, area, and orientation and are embedded within a single crystal silicon wafer. Two processes for growing opal-patterned chips are described. One is based upon microfluidic and the other spin coating driven self-assembly of colloidal silica micro-spheres within a lithographic patterned silicon wafer.

1. Three-Dimensional Photonic Crystals and Omnidirectional Photonic Bandgaps

New methods are emerging for miniaturizing and integrating optical components into compact functional systems offering high processing speeds.[1] Optical analogues to the planarization and integration of microelectronic devices into silicon, provide the potential to develop a rival technology. The evolution of photonics will depend on the development of photonic materials that enable the generation, localization, detection, amplification, and processing of light by microphotonic devices.[2] A new material (device) that could prove useful in this regard is the three-dimensional photonic crystal (3D PC). The defining feature of a 3D PC is the periodicity of dielectric material along all spatial directions.[3] A 3D PC sculpted in silicon is shown in Figure 1. 3D photonic lattices have the property of diffracting light according to Bragg's law. For the fcc structure of air holes in silicon shown in Figure 1 a refractive index contrast (RIC) greater than 2.85 is required to create a complete photonic bandgap (PBG) in the photon density of states (PDS). This results in the inability of light to be coupled into and propagate within the PC in any direction at wavelengths corresponding to the PBG.[4] It is the PBG that enables the PC to manage photons in ways like semiconductors manipulate electrons. By engineering the lattice dimensions of the PC it could potentially be designed to function as either a passive or active photonic device that operates in the near infrared around 1.5 μm, the wavelength most often used in optical telecommunication systems.

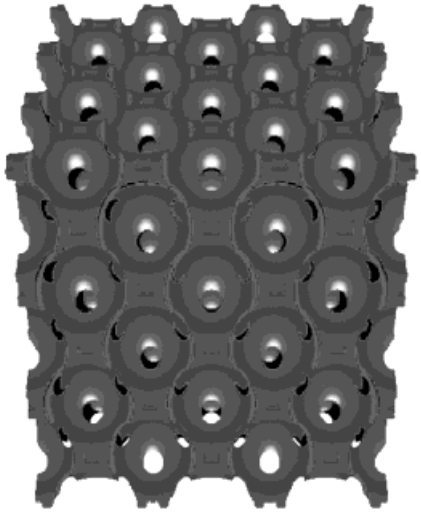


Figure 1. A 3D PC comprised of a fcc lattice of micrometer scale air holes cast in silicon. Graphical image reproduced with permission Ovi Toder, Department of Physics, University of Toronto.

2. Photonic Crystal Theory

Ideas about PCs originated more than a decade ago with the theoretical work of Yablonovitch and John.[5,6] Their theory of PCs is founded upon the scattering and interference of light in

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a periodic dielectric at wavelengths comparable to the lattice spacing of the PC. Theory shows that forbidden frequencies for the propagation of light in the PC, known as the PBG, result from the interplay of Mie scattering and Bragg interference of light, Figure 2.[7] The existence of a PBG causes selective filtering of certain wavelengths of light while other wavelengths are transmitted. In order to obtain experimental evidence of a complete PBG in 3D PCs, much effort has been directed towards chemical synthesis and engineering physics ways of fabricating materials with topologically complex 3D constructions expected to show the effects of a PBG. Evidence being sought to prove the existence of an omni-directional PBG include exclusion and localization of light as well as inhibition of spontaneous emission in all spatial directions within the PBG, however research of this kind is still in its infancy. This is mainly because of the technical difficulty of producing high quality 3D single crystal photonic lattices in high RIC materials. To be useful, these kinds of periodic dielectrics need to be constructed of regular arrays of building blocks with dimensions of the order of the wavelength of near infrared light, high RIC, and sufficiently free of imperfections to be able to manifest and detect optical phenomena expected for a photonic crystal with a complete PBG.[4]

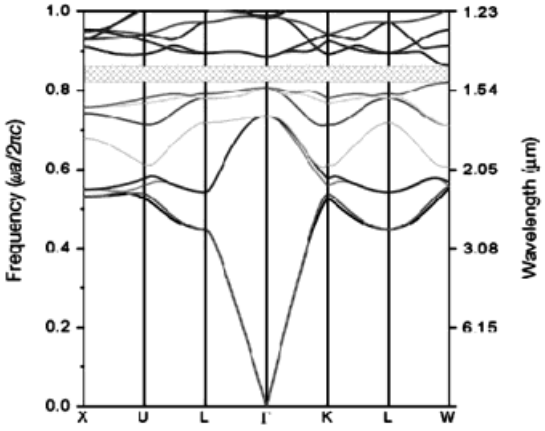
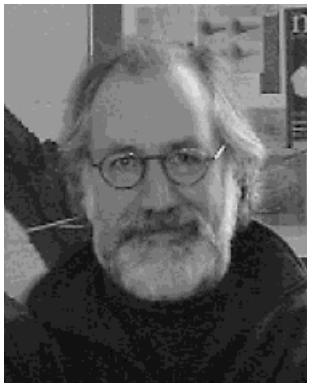


Fig. 2. Calculated optical band structure of a 3D PC having the fcc structure of air holes in silicon depicted in Figure 1 [13]. Reproduced with permission from Macmillan Publishers Ltd (copyright 2000).

3. Photonic Crystal Technology

Progress with 3D PCs targeted at photonic chip technology will ultimately rest on the ability to planarize and integrate PC devices into flat substrates. In addition it will be important to control and understand how imperfections in 3D PCs influence the PBG and their ability to confine photons in all spatial directions of the Brillouin zone, Figure 2. The scanning electron microscopy (SEM) image shown in Figure 3 depicts imperfections typically found in a synthetic opal known as a silica colloidal crystal, a material currently used to template a 3D PC. Crystal imperfections, such as site vacancies, dislocations, and stacking faults, size, shape, and positional disorder and fracture lines in a photonic lattice lead to a reduction or closing of PBGs and disrupt the efficacy of 3D PCs to reflect, transmit, localize, slow or guide light. In addition, calculations have



Geoffrey A. Ozin received a B.Sc. first class special honours degree in chemistry from Kings College University of London in 1965 and a D.Phil. degree in inorganic chemistry from Oriel College Oxford University in 1967. He was an ICI Fellow at the University of Southampton from 1967–69 before joining the University of Toronto in 1969. He achieved the rank of full professor in 1977 and Canada Research Chair in Materials Chemistry in 2001. He has published around 450 articles and obtained 14 U.S. patents. His materials chemistry research group uses self-assembly methods to organize inorganic, organic, and polymeric building units into materials. The group's synthetic methodologies embrace concepts in molecular and supramolecular templating, colloidal and layer-by-layer assembly, soft-lithography and host-guest inclusion, crystal engineering, and biomimetic chemistry.

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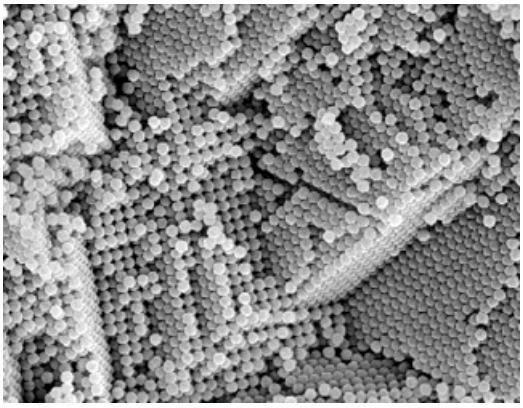

Fig. 3. SEM image of a silica colloidal crystal, which depicts various kinds of structural imperfections [16]. Reproduced with permission from the American Chemical Society.

shown that polydispersity greater than 2–5% is sufficient to degrade or close the complete photonic bandgap.[8] It is likely that for the real potential of 3D PCs to be realized, the effects of inherent defects and randomness in the photonic lattice will need to be minimized. The next step is to learn how to incorporate specific structural defects in order to achieve a particular function. The control of structural defects in 3D PCs, such as points, lines, and bends, together with internal light sources, is likely to facilitate the generation and confinement of photons in 3D photonic lattices. This could enable the development, for example, of zero-threshold micro-lasers and micro-circuits, for generating and guiding light between PC devices, such as optical switches, wavelength dispersion compensators, and wavelength division multiplexers. These possibilities, if reduced to practice, could potentially lead to a photonics technology with integrated PC devices coupled to optical fibers in all-optical microphotonic circuits, computer and telecommunication systems.

4. Self-Assembly and Fabrication of 3D Photonic Crystals

Presently, three main methods are providing the first examples of sufficiently high quality 3D photonic lattices in the form of crystals and films, for optical studies and, the construction and evaluation of the performance of PC devices. These methods comprise micro-machining,[9] holographic photolithography,[10] and colloidal assembly.[11] Each approach has strengths and weaknesses, which are in the process of being defined and evaluated. It is not clear whether one or a combination of the methods of physically sculpting and chemically shaping materials into 3D PCs will dominate in this emerging field

In order to realize the full potential of 3D PCs for practical device applications it is generally agreed that a minimum of four criteria need to be satisfied. These include: i) a complete PBG in the PC in the near infrared wavelength region, ii) controlled introduction at specified positions of point, line, or bend defects into the PC, iii) an efficient light-emitting element in the PC, and iv) electronically conducting PC-active interfaces. A recent example of a 3D PC that satisfies all four of these criteria is a microfabricated Lincoln Log architecture in which structural defects have been micromachined into a high refractive index III–V semiconductor. These structures have been demonstrated to have an omni-directional PBG in the near infrared and can guide and bend light in engineered structural defects.[12] Another example exploits tunable interference patterns of multiple laser beams that can be generated and replicated within a photosensitive polymer to form 3D polymeric photonic lattices with a wide variety of network topologies. Holographic photolithography of this type creates templates for making PC facsimiles in high RIC inorganic materials like titania.[10] Complete PBGs have yet to be demonstrated in these photonic materials.

Such physical methods for shaping semiconductors into PCs generally involve complex, time consuming, expensive, and multi-step processing, not available in ordinary laboratories. By contrast, the self-assembly of monodisperse micrometer scale silica spheres into face-centered cubic (fcc) colloidal crystals provides a simple, fast, and cheap materials chemistry approach to PCs.[13] To make these kinds of PCs, a sintered silica colloidal crystal has been used as a template to replicate the interstitial void space, in the form of a high refractive index material, such as silicon, $\eta = 3.45$.[13] The high temperature sintering procedure creates necks (connecting points) between adjoining silica micro-spheres, which provides mechanical stability to the template, the ability to deposit silicon inside the template using chemical vapor deposition (CVD), and subsequently extract the silica template to leave behind a 3D silicon PC with a network topology that displays a complete PBG, Figures 1, 2, and 4. The silicon PC obtained in this way appears to be impenetrable to near infrared light around 1.5 μm, the wavelength of choice for glass fiber optic communications, although proof of a complete PBG in these PCs will require

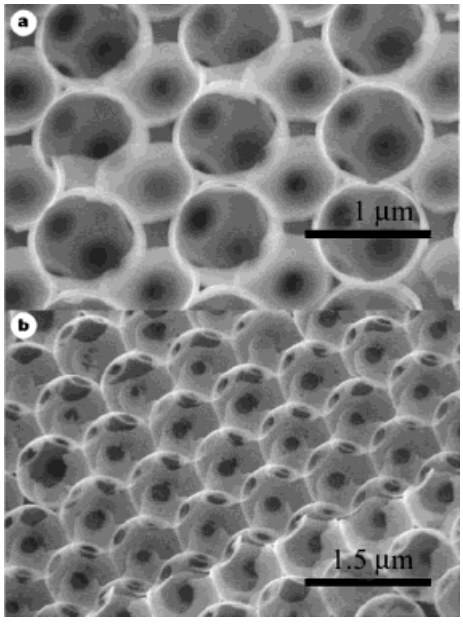

Fig. 4. SEM image showing the structure of an opal templated 3D silicon PC [13]. Reproduced with permission from Macmillan Publishers Ltd (copyright 2000).

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detailed angle dependent optical reflectivity studies.[13] Colloidal crystal templating of PC can be generalized to a range of other high refractive index semiconductors to allow engineering of the PBG.

5. The Three-Dimensional Photonic Crystal Challenge

A contemporary challenge in the field of 3D PCs is to find a straightforward, fast, reproducible, and inexpensive way to pattern defect-free opals in silicon wafers—coined the opal-patterned chip. Key targets to be achieved in the opal-patterned chip include control of the thickness, area, orientation, and registry of single crystal colloidal crystals inside an oriented silicon substrate. Such constructions could function as templates for synthesizing planarized and integrated silicon 3D PC devices, inside silicon chips, having an omni-directional PBG near 1.5 μm. Two directed self-assembly approaches to this technical challenge combine microfluidics and spin coating with colloidal assembly and soft lithography. These approaches have recently been developed in our laboratory,[14] and are the central focus of this article. To place this work in perspective, the following paragraphs examine earlier attempts to assemble and pattern high quality colloidal crystals and films.

6. Colloidal Crystals and Films

Dip-coating,[15] sedimentation,[16] and specially designed micro-cells[17] represent several methods of crystallizing mono-disperse micro-spheres into colloidal crystals and films. In order to make silicon 3D PCs with a PBG in the near infrared, micro-spheres made of silica with sizes greater than 850 nm are required. Such large micro-spheres have proven to be difficult to synthesize, make mono-disperse, and organize into well ordered lattices.[13] Colloidal crystals and films as well as their inverted replica materials that have been synthesized to date display various kinds of disorder, which arise from sphere size polydispersity, site randomness, intrinsic point, line and planar defects, polycrystalline domains, fracture cracks, inhomogeneity in filling and refractive index contrast, and the presence of mixtures of amorphous and crystalline phases. The "defect tolerance" of colloidal crystals on properties such as completeness of PBGs in PCs is a topic of intense current interest.[8]

7. Colloidal Crystals within Substrates

Before our work on microfluidic and spin-coating assembly of planarized single crystal colloidal crystals patterned within oriented silicon substrates,[14] solvent assisted micromolding in capillaries (MIMIC),[18] electrostatic assembly,[19] and micro-robotic[20] techniques have been used to pattern mono-disperse micro-spheres on top of various substrates.[21] Micro-spheres organized in these ways sometimes require long preparation times and special instrumentation and are unable to simultaneously control order, defects, area, thickness, topology, orientation, and registry of patterned colloidal crystals. Also, colloidal crystals prepared in these ways usually display an fcc lattice oriented in the (111) direction. Colloidal crystals displaying a specific (100) orientation have been grown by sedimentation of micro-spheres onto a lithographic patterned substrate, a technique known as colloidal epitaxyi[22a] however, epitaxial growth of a colloidal crystal film is slow and structural order is limited to layers close to the lithographically patterned substrate. Recently, Crocker and co-workers reported the growth of colloidal crystals in the (100) direction through entropy-driven crystallization of micro-spheres on a patterned poly(methylmethacrylate) (PMMA) substrate.[22b] As described below, opal chip self-assembly inside planar substrates using microfluidic and spin-coating methods offer possibilities to circumvent most of the aforementioned difficulties, and in a facile, quick, and cheap process creates "wafer-packaged 3D diffractive optic elements".

8. Microfluidic Colloidal Crystal Self-Assembly

It is well documented that soft lithography encompasses a suite of methods that are useful for the fabrication of micrometer to sub-micrometer scale patterns on a range of planar and curved substrates.[23] The procedures are conducive to working in an ordinary laboratory environment. We have used soft lithography coupled with microfluidic colloidal crystal self-assembly to grow opal-patterned silicon chips, Figure 5.[14] A line patterned polydimethylsiloxane (PDMS) master is obtained by casting a pre-polymer gel from the corresponding lithographically defined photo-resist pattern.

A procedure for fabricating patterns of V-shaped grooves inside a Si(100) wafer begins with a PDMS master that is inked with an alkanethiol in ethanol and then printed onto a Au coated Si(100) wafer having a titanium adhesion layer. The bare gold surface is then removed with a cyanide etching solution, and the underlying Si(100) substrate is then anisotropically etched in base to give V-shaped grooves with 70.6° apex angles beneath the surface of the wafer, as seen in the SEM image in Figure 6. A flat PDMS block is next put into conformal contact with the patterned wafer and a drop of an aqueous dispersion of monodisperse silica micro-spheres (diameter = 840 ± 20 nm) was added at the interface between the patterned silicon wafer and the block.[23]

Micro-spheres are rapidly driven into the V-shaped grooves by capillary forces and close-pack inside the grooves upon evaporation of the water-dispersing agent. Due to the 70.6° angular geometry of the V-shaped grooves, micro-spheres collect and self-assemble in a vectorial fashion exclusively within the grooves to form the desired pattern of fcc colloidal crystal parallel lines. This can be seen in the SEM images shown in Figures 7–9. It is noteworthy that {100} layer planes are well ordered and organized parallel to the [100] face of the single crystal Si(100) wafer. Over spatial areas sufficiently large (5–10 unit cells) for construction of photonic crystal micro-devices, colloidal crystals are seen to form single crystals and can be made essentially free of defects, Figures 7. A measure of defect

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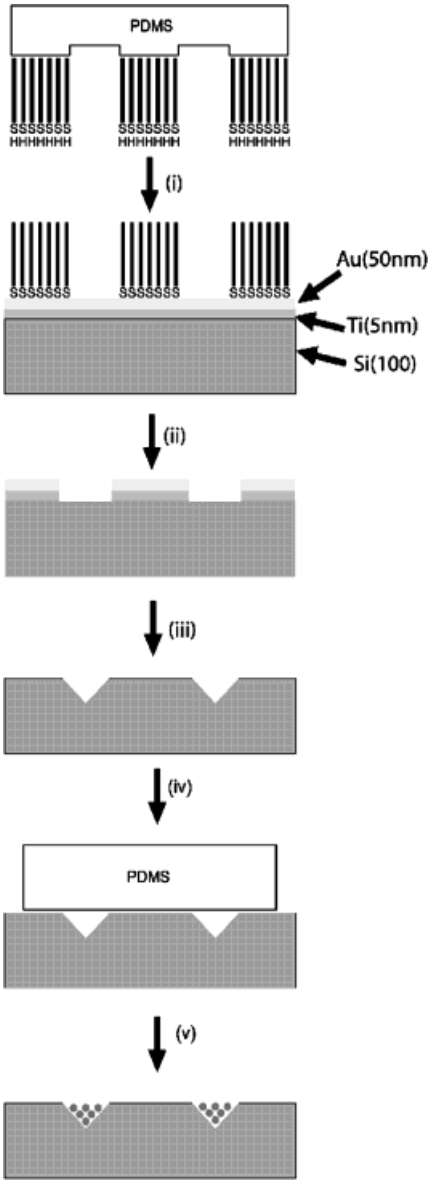

Fig. 5. Microfluidic colloidal self-assembly. Synthetic scheme illustrating vectorial control of thickness, area, orientation, and registry of silica colloidal crystals in silicon wafers.

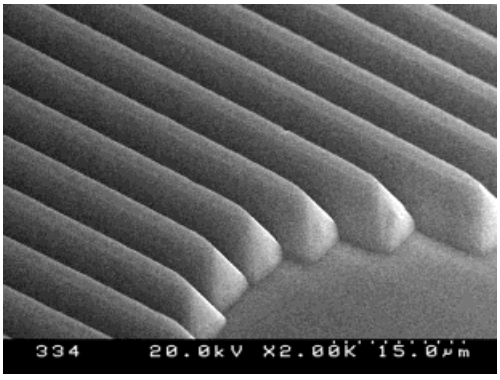

Fig. 6. SEM image of anisotropically etched V-shaped channels inside an Si(100) wafer obtained using soft lithography [14]. Reproduced with permission from the Royal Society of Chemistry (copyright 2000).

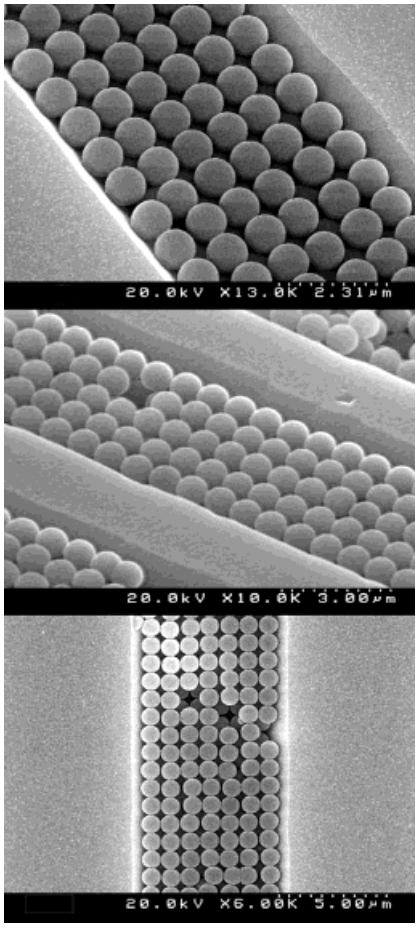

Fig. 7. SEM images depicting top: six-layer (100) single crystal silica colloidal crystal in V-shaped channel of Si(100) wafer and devoid of vacancy defects. Middle: five-layer (100) single crystal silica colloidal crystal in V-shaped channel of Si(100) wafer depicting single vacancy defects in the top layer of micro-spheres. Bottom: seven-layer (100) single crystal silica colloidal crystal in V-shaped channel of Si(100) wafer depicting three vacancy-type defects in the top layer of micro-spheres, [14]. Reproduced with permission from the Royal Society of Chemistry (copyright 2000).

density remains to be defined. When micro-sphere vacancies are present in the silica colloidal crystals this provides an opportunity to study them by a combination of confocal optical and electron microscopies and single domain optical diffraction. In this way, the effect of different numbers, locations, and arrangements of point defects on optical diffraction properties may in principle be evaluated. Details of these studies when completed will be reported later.[24]

Interestingly, the first micro-spheres observed to nucleate in the V-shaped grooves are single-file contiguous arrangements. These linear constructions are found to be located in the apex of the V-shaped groove, Figure 9. The 1D chains of micro-spheres dominate in the early stages of microfluidic colloidal assembly inside the silicon V-shaped channels and when dilute aqueous dispersions (ca. 0.05 wt.-%) of micro-spheres are used. At later stages the micro-spheres self-assemble adjacent to the 1D chains and continue to grow up the walls of the V-shaped grooves to eventually fill them with colloidal crystals, Figure 8. Furthermore, the observed registry of {100} layer planes of micro-spheres between adjacent grooves provides additional

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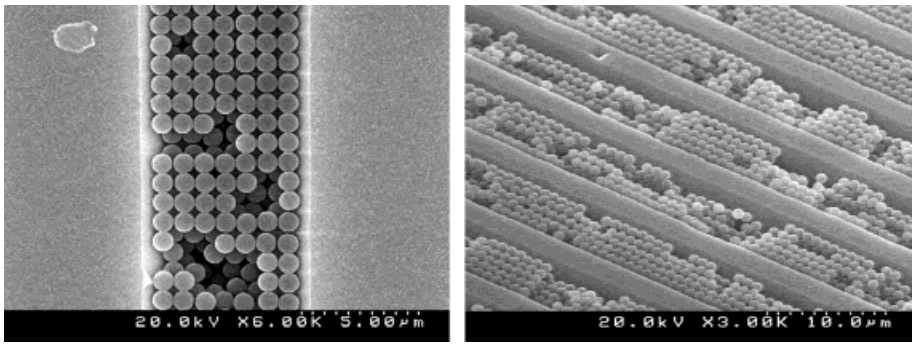

Fig. 8. Left: Top SEM view of a seven-layer stack of well-ordered silica micro-spheres inside V-shaped grooves of Si(100) depicting selective growth of the silica colloidal crystal along the (100) direction. Right: Lateral SEM view showing vectorial (100) growth and registry between a collection of well-ordered silica colloidal crystals within parallel V-shaped grooves in Si(100) [14]. Reproduced with permission from the Royal Society of Chemistry (copyright 2000).

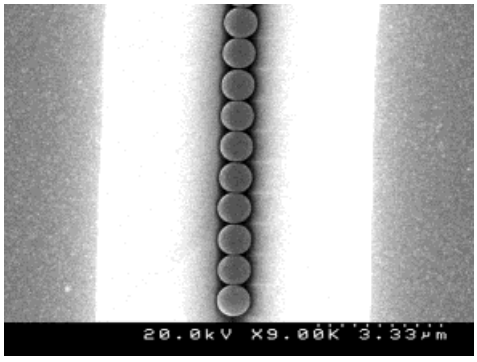

Fig. 9. SEM image showing formation of a 1D chain of silica micro-spheres grown in the apex region of a V-shaped groove, anisotropically etched within the surface of a single crystal (100) silicon wafer [14]. Reproduced with permission from the Royal Society of Chemistry (copyright 2000).

evidence for vectorial control of the colloidal crystal nucleation and growth. This sequence of steps may provide insight into the mechanism that enables control of thickness, area, orientation, and registry of the patterned silica colloidal crystal within the confined space of V-shaped channels in the silicon wafer. The whole process outlined above is reproducible and can be completed in less than 2 h. The actual capillary infiltration and crystallization of micro-spheres in the patterned silicon wafer can be as short as seconds to minutes and the entire assembly process is restricted just to the areas defined by the V-shaped channels. As the depth of the V-shaped grooves in Si(100) is proportional to the etching time, it is easy to control groove depth to accommodate a predetermined number of layers of silica micro-spheres. This has been achieved for one to ten layers of patterned silica colloidal crystals and the method works well for both large 840 nm and small 300 nm micro-spheres and is not restricted to silica, latex spheres behave well too. Note that the number of micro-spheres observed in the top (100) layer corresponds to the number of micro-sphere layer planes of the colloidal crystal within the V-shaped grooves.

9. Spin-Coating Colloidal Crystal Self-Assembly

As delineated above, opal-patterned chip preparation by an amalgamation of microfluidics, colloidal self-assembly, and soft lithography,[14] has the potential to circumvent some of the difficulties encountered in earlier attempts to make high quality colloidal crystals. However, a limitation of this new method of assembling opal-patterned chips is the restriction of the growth of colloidal crystals within the spatial confines of open and continuous channels etched inside the substrate. The open and continuous nature of the channels is a prerequisite to enable capillary-pressure-driven influx of suspensions of micro-spheres into the channels to facilitate crystallization of the micro-spheres into predetermined colloidal crystal lattice structures and patterns. Complete filling of the channels with a colloidal crystal can prove difficult because of channel plugging problems during capillary driven infiltration of suspensions of micro-spheres. Spin-coating colloidal self-assembly circumvents these impediments allowing micro-spheres to crystallize into controlled thickness, area, orientation and registered opal patterns within closed and finite shaped pits inside the substrate.

The procedure for fabricating an array of square pyramid-shaped etch pits, inside a Si(100) wafer begins with a line patterned PDMS master that is inked with an alkanethiol in ethanol. The inked master is then printed twice, mutually at right angles, onto an Au-coated Si(100) wafer having a titanium adhesion layer. The bare gold surface is then removed with a cyanide etching solution, and the underlying Si(100) substrate is then anisotropically etched in aqueous base.[23] This preferentially exposes (100) surfaces and thereby gives square pyramidal-shaped etch pits with adjacent walls mutually inclined at 70.6° angles beneath the surface of the wafer, as seen in the SEM image in Figure 10. The same square pyramidal pattern of etch pits can be obtained in a single alkanethiol inking process but instead using a square grid PDMS master.

Once the patterned silicon substrate has been fabricated using soft lithography, a dispersion of monodisperse silica micro-spheres (840 ± 20 nm) is placed on top of the patterned wafer and supported on the chuck of a conventional spin-coat-

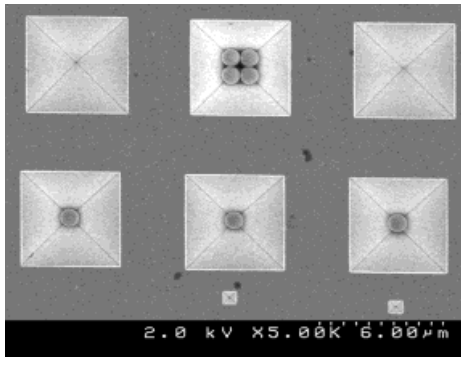

Fig. 10. SEM image of a representative example of anisotropically etched square pyramid-shaped pits inside a Si(100) wafer obtained using soft lithography and spin-coating deposition of small numbers of silica micro-spheres exclusively within the etch pits.

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er. By subjecting the wafer to a specified (see below) spinning program the micro-sphere suspension is driven horizontally and at a controlled rate across the surface of the wafer by centrifugal forces. During this process of centrifugal spreading of the micro-sphere suspension uniformly across the surface of the silicon wafer patterned with a predetermined array of etch pits, the micro-spheres are subjected to a combination of gravity driven sedimentation, and evaporation-induced capillary forces. Together, these forces cause the micro-spheres to rapidly settle, self-assemble, and crystallize in the etch pits. The spinning program is key to ensuring the colloidal crystals grow exclusively in the etch pits rather than on the top surface of the wafer, Figures 10 and 11. To amplify, low spinning speeds (500–1000 rpm) are first used to spread the micro-sphere suspension evenly across the wafer and crystallize them in the etch pits. This process is then followed by high spinning speeds (1500–2000 rpm) to remove excess micro-spheres that deposit on the surface of the wafer. This procedure and combination of physicochemical effects causes the micro-spheres to deposit and close-pack in an orderly fashion within the etch pits inside the substrate. Due to the 70.6° angular geometry of the square pyramid-shaped pits, micro-spheres nucleate and grow in a vectorial fashion exclusively within the pits to form a pattern of fcc colloidal crystals. This can be controlled to yield the desired degree of filling and number of micro-sphere layer planes within the etched pits, as can be seen in the SEM image shown in Figure 12 for the growth of four layer-planes of silica microspheres within a closed finite size square pyramid-shaped etch pit inside oriented (100) silicon. It is noteworthy that the {100} layer planes of the silica colloidal crystal are well ordered and organized parallel to the [100] face of the single crystal Si(100) wafer. Over spatial areas of 5–10 unit cells colloidal crystals are found to be single crystals (Fig. 12). When micro-sphere vacancies or extra micro-spheres are present in the surface regions of the in-wafer silica colloidal crystals they can easily be identified by SEM (Fig. 13). Exploration of "hidden defects" in the bulk regions of the in-wafer silica colloidal crystal requires the use of confocal and electron microscopy, studies that are currently underway.

Interestingly, the first micro-spheres observed to nucleate in the square pyramidal-shaped etch pits are singlet, duplet, triplet, and quadruplet arrangements of micro-spheres located at the apex of the square pyramid-shaped pit, examples being shown in Figure 10. These embryonic "microsphere clusters" are found to dominate in the early stages of the spin coating colloidal self-assembly process inside the silicon etch pits and when dilute aqueous dispersions (0.05 wt.-%) of micro-spheres are used. At later stages and with more concentrated suspensions (2 wt.-%), micro-spheres close-pack always starting from the apex and continue to grow up the edges and walls of the square pyramid-shaped etch pit to eventually fill them with well-ordered patterns of silica colloidal crystals, Figure 11. The space that remains in the etch pit, is subsequently filled with well-ordered close-packed micro-spheres. Further, the observed registry of {100} layer planes of micro-spheres between adjacent pits provides evidence for vectorial control of colloidal crystal nucleation and growth.

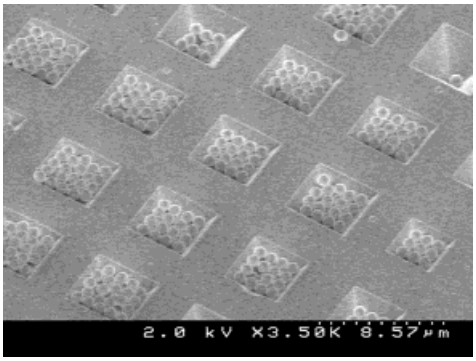

Fig. 11. Low magnification SEM image depicting the outcome of spin coating colloidal self-assembly of silica micro-spheres, inside square pyramid-shaped, etch pits in an oriented (100) silicon wafer.

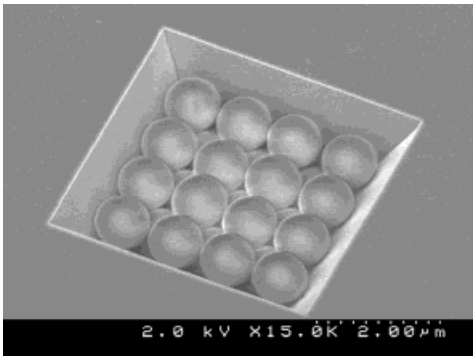

Fig. 12. SEM image depicting four layer-planes of single crystal (100) oriented silica colloidal crystal grown within square pyramid-shaped, etch pits inside an oriented (100) silicon wafer by spin coating colloidal self-assembly.

The whole process outlined above is reproducible and can be completed in less than 2 h and the etch pits can be completely filled with well-ordered close-packed colloidal crystals. The spin coating and crystallization of micro-spheres in etch pit patterned silicon wafers take as little as seconds to minutes and the

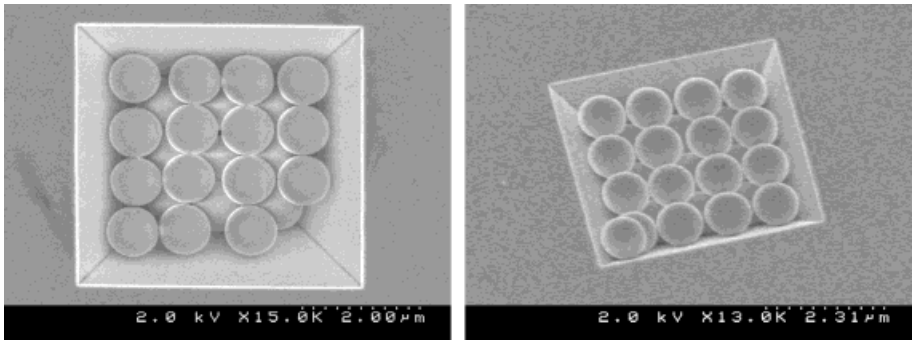

Fig. 13. SEM images depicting four layer-planes of single crystal (100) oriented silica colloidal crystal containing a single micro-sphere vacancy defect (left) and an extra micro-sphere (right), grown within square pyramid-shaped, etch pits inside an oriented (100) silicon wafer by spin coating and colloidal self-assembly.

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entire colloidal crystallization process is restricted just to the areas defined by the pits. This arises because any micro-spheres remaining on the surface of the wafer after colloidal crystallization in the etch pits using slow spinning are subsequently thrown outwards and off the wafer at fast spinning rates by centrifugal forces. As the depth of the pits in Si(100) is proportional to the etching time, it is easy to control pit depth to accommodate a predetermined number of layers of micro-spheres.

Another attractive and novel feature of the spin-coating colloidal self-assembly process performed on patterned silicon wafers is the ability to tune the structure of the colloidal crystal grown inside the closed etch pits within the wafer. This observation stems from observations of the effect of the geometry of the etch pits on nucleation and growth of the colloidal crystal within the pits. To amplify, the first micro-spheres to settle in a rectangular pyramid-shaped etch pit usually locate on the apex line, Figure 14. Hence the number and geometry of this microsphere arrangement depend on the relative sizes of the microsphere diameter and length of the line that defines the apex of the rectangular pyramid-shaped pit. If the arrangement is "commensurate", that is, the apex line is an integral number of microsphere diameters then the expected fcc colloidal crystal oriented along the (100) will grow in the rectangular pyramid-shaped etch pit as seen in Figure 15. By contrast, if the arrangement is "incommensurate", that is, the apex line is a non-integral number of micro-sphere diameters then the first micro-sphere(s) to settle in this kind of rectangular pyramid-shaped etch pit will not fit exactly on the apex line. Under these circumstances, non-fcc packing arrangements of micro-spheres, whose structures remain to be established, are observed to grow inside the pits, Figure 16. The colloidal crystal lattice structure and orientation that nucleates and grows within the etch pit, then appears to depend upon the ratio of the lengths of the sides of the rectangular pyramid-shaped etch pit. Therefore, the attainable precision in the diameter of the micro-spheres from chemical synthesis and the accuracy of the pit dimensions from the lithographic processes become important colloidal crystal structure determining factors. The structure of the colloidal crystal may also depend on competitive surface interactions of micro-spheres with micro-spheres versus micro-spheres with the walls of the etch pit in the wafer.

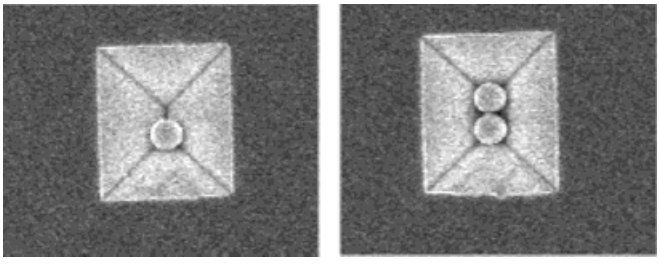

Fig. 14. SEM images of singlet (left) and duplet (right) arrangements of silica micro-spheres grown by spin coating inside a rectangular pyramid-shaped, etch pit within an oriented Si(100) wafer.

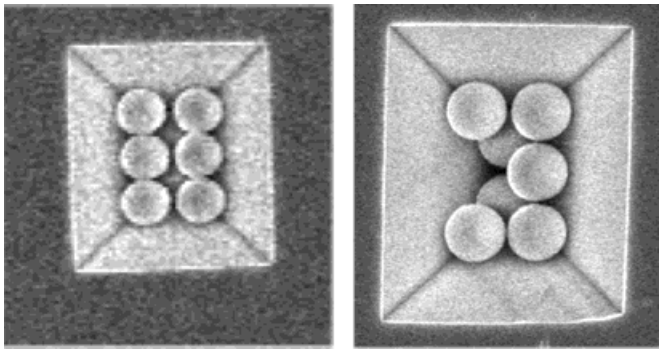

Fig. 15. SEM images depicting two layer-planes of a "commensurate" (100) oriented single crystal silica colloidal crystal, one of which contains a single vacancy defect, grown within a rectangular pyramid-shaped etch pit inside an oriented (100) silicon wafer by spin coating colloidal self-assembly.

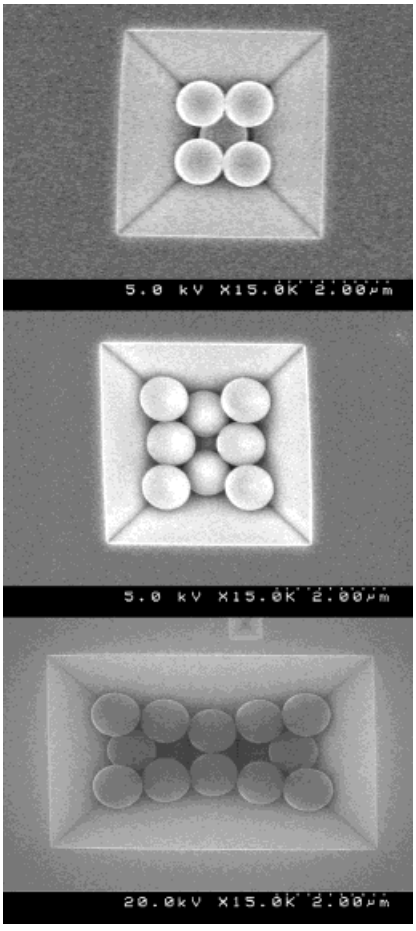

Fig. 16. SEM images depicting "incommensurate" silica colloidal crystals grown inside a rectangular pyramid-shaped etch pit, within an oriented (100) silicon wafer by spin coating, colloidal self-assembly.

These observations suggest that "made-to-measure" colloidal crystals patterned inside planar substrates can be designed by intentional selection of the commensurate or incommensurate nature of rectangular pyramid-shaped etch pits inside oriented Si(100) wafers, Figure 17. Further, with judicious choice of the chemical funtionalization of surfaces of the microspheres and walls of the etch pits it could be possible to tailor new kinds of colloidal crystal structures. This is significant because the thermodynamically stable structure of close-packed micro-spheres is fcc. Since the inception of the field of colloidal crystallization it has so far proven impossible to gain command

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ADVANCED FUNCTIONAL MATERIALS

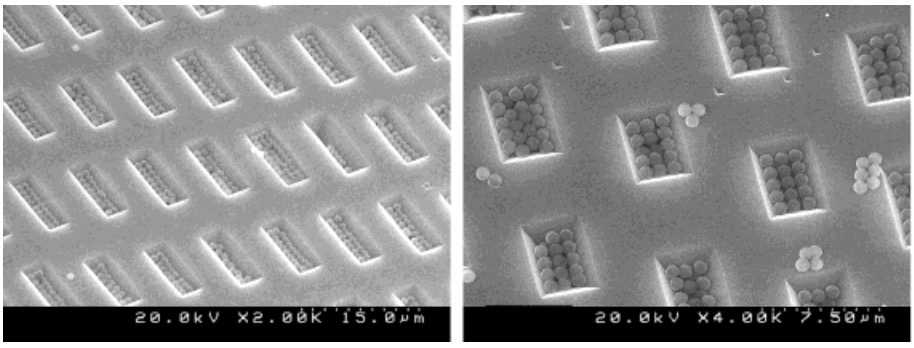

Fig. 17. Low magnification SEM image depicting the outcome of spin coating colloidal self-assembly of silica micro-spheres, inside rectangular pyramid-shaped etch pits having different orthogonality in an oriented (100) silicon wafer.

over colloidal crystallization of lattice types other than fcc, such as body-centered cubic, hexagonal close-packed, tetragonal, or diamond. The capability to design both the topology and orientation of the colloidal crystal lattice having controlled thickness, area, and registry inside silicon wafers has potential for tuning photonic bandgaps, band structure, and density of states for 3D PCs and devices. The most desirable target would be an opal-patterned chip with the diamondoid lattice. This would provide access to diamondoid-based PC devices, which are predicted[3] to have one of the largest attainable and most defect-tolerant PBGs at the pivotal wavelength of around 1.5 μm.

10. Conclusion and Outlook

In this article we have described two new processes based on directed self-assembly for synthesizing opal-patterned chips—single crystal silica colloidal crystal designs within oriented silicon wafers. These approaches integrate methods in microfluidics and spin coating with colloidal self-assembly and soft-lithography to create micrometer scale opal-patterned chips. Opal-patterned chips have been made with a sufficiently high degree of colloidal crystal structural perfection to make them suitable as potential templates for constructing integrated 3D silicon PC devices. Micro-sphere sizes can be tuned and structures can be made of a sufficient number of unit cells, to be of interest in the development of 3D PC devices.

There is still much work to do, especially with respect to the control of intrinsic defects and incorporation of extrinsic defects like points, lines, and bends. For instance, there could be all kinds of defects hidden below the surface of opal-patterned chips and their presence or absence and effects on photonic crystal properties need to be investigated and defined. Studies underway to further elaborate these issues include single domain optical diffraction, confocal microscopy, and electron microscopy. Unpublished work on our opal chips show that colloidal crystals grown in silicon wafers display the theoretically predicted optical diffraction expected for single crystal colloidal crystals.[24]

The work described in this paper, enables optical band structure engineering and spatial and angular resolved optical diffraction studies, to be performed on in-wafer single crystal colloidal crystals. Other opportunities include inversion of the opal patterns on the chip in a range of inorganic and polymeric compositions, the incorporation of extrinsic structural defects, internal light sources and smart (e.g., electrically, magnetically, optically, thermally, and pressure tunable PBGs) materials in the opal-patterned and inverse opal-patterned chips and evaluation of their effect on photonic crystal properties. Building opal chips via straightforward directed self-assembly methods such as those outlined in this paper could provide an enabling technology for the manufacture of photonic chips that integrate optical fibers, waveguides, 3D PCs and wafers for all-optical chips, computers, and telecommunication systems, Figure 18.

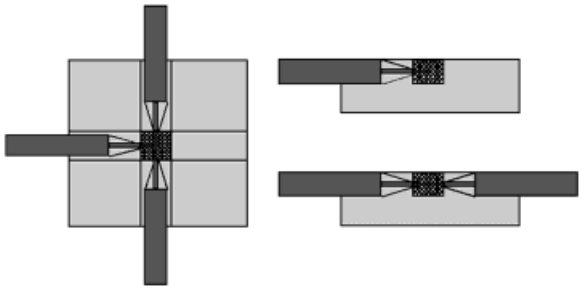

Fig. 18. Illustration of a possible futuristic photonic chip: optical fibers couple light into and out of an in-wafer self-assembled PC.

It remains to be seen whether the methods described here will compete with 3D PCs fabricated by physical sculpting approaches involving multi-step photolithography, etching and wafer bonding, focused ion-beam or holographic photolithography.[9,10,12,25]

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